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NONADIABATIC PROCESSES RELEVANT to HEDMS and ATMOSPHERIC CHEMISTRY

David. R. Yarkony
Department of Chemistry
Johns Hopkins University
Baltimore, MD 21218

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STATUS OF EFFORT/ ACCOMPLISHMENTS/ NEW FINDINGS/FUTURE DIRECTIONS

A. Overview

Our research program focused on aspects of nonadiabatic chemistry that are relevant to Air Force missions including the spectra of potential high energy density materials (HEDMs); reactions in the upper reaches of the earth's atmosphere; and the quantitative detection of species relevant to iodine based energy transfer chemical lasers. We considered the spectra of the polynitrogen compounds, $(CH)_nN_{5-n}$ which can be viewed as nitrogen substituted cyclopentadienyl radicals; the reaction of $O(^3P)$ with H_2O which is relevant to uV signatures of rocket engines; began a collaborative effort with Hans Lischka's group (Vienna) and Ron Shepard's group (Argonne) to extend the capabilities of COLUMBUS to include our algorithms for describing the electronic structure aspects of electronically nonadiabatic processes, including algorithms for determining the derivative coupling, and for locating and analyzing two state and three state conical intersections. COLUMBUS, a state-averaged multiconfigurational self-consistent field / configuration interaction based, system of electronic structure codes can utilize either sequential (single processor) or parallel (multiprocessor) architectures and will significantly increase both the range problems in nonadiabatic chemistry accessible to treatment and the accuracy of those treatments. Further since COLUMBUS is freely available from the website <http://www.itc.univie.ac.at/~hans/Columbus/columbus.html> the capabilities for treating nonadiabatic processes we have developed over the past decade will be made available to the general scientific community.

Using the COLUMBUS codes we carried out very accurate calculations of the quadrupole transition moment for the $a^1\Delta \rightarrow b^1\Sigma^+$, transition in NCl and in O_2 . The O_2 result was used by Skip Williams of AFGL to develop a quantitative detector for $O_2(a^1\Delta)$. Our NCl results will be used for a similar purpose.

However while the O_2 and NCl calculations were of significant practical importance in the design of chemical laser systems based on O_2 or NCl, the result with perhaps the greatest long term implications was our determination that conical intersections of three electronic states of the

same symmetry impact the ground electronic state of the substituted cyclopentadienyl radical, pyrazolyl radical, $(CH)_3N_2$, exist for the remaining homologues, $(CH)_{5-n}N_n$, $n = 1, 2$, and 4 and are particularly low-lying in the triazolyl, $n = 3$, geometrical isomers. These studies complement experimental studies in W. Carl Lineberger's laboratory of the doublet radicals $(CH)_{5-n}N_n$, $n = 1, 2, 3, 4$. Our calculations suggest that conical intersections of three states of the same symmetry, virtually ignored in the past, are likely to exist in many organic radicals.

In future work we will use algorithms currently being developed in our laboratory to determine the impact three state intersections have on the observed spectra. We will also develop algorithms to treat the electronic structure aspects of the energy transfer reactions, $I + XY^* \rightarrow I^* + XY$, where $XY = O_2$ or NCl , which are relevant to chemical iodine laser systems. Our approach will differ significantly from previous work in that we will determine and characterize the relevant conical intersections *including* both the spin-orbit interaction and the effects of time reversal symmetry.

B. Scientific Software

(i) COLUMBUS 5.9

One of the goals of our research program has been to make the tools we have developed for locating, describing and analyzing conical intersections freely available to the general scientific community. In addition we would like to extend the range of accessible problems by taking advantage of the enormous power of parallel computing. To accomplish these goals a collaboration has been established, with Hans Lischka's group (Vienna) and Ron Shepard's group (Argonne), developers of the COLUMBUS suite of electronic structure programs. COLUMBUS is a state of the art, highly efficient, state-averaged multiconfigurational / multireference configuration interaction wave function based system of computer codes¹ which runs on both sequential (single processor) and parallel (multiprocessor) platforms and is freely available from the website <http://www.itc.univie.ac.at/~hans/Columbus/columbus.html>. As a result of our collaboration COLUMBUS version 5.9 now has algorithms for (i) for the determining the derivative couplings the interactions that couple the adiabatic electronic states, and (ii) locating two state and three state

conical intersections. In the future we will be adding to COLUMBUS our suite of tools for analyzing conical intersections and searching for and characterizing confluences. The calculations performed on pyrazolyl, O₂ and NCl, described below, would not have been possible without the enhanced capabilities of the COLUMBUS codes.

COLUMBUS will both increase the range of accessible problems in nonadiabatic chemistry and provide access to these tools for the general scientific community.

(ii) Dynamics Near Conical Intersection

A second goal of our software development program is to be able to study nuclear dynamics near conical intersections. This capability will enable us to model the photoelectron spectra of molecules based on our electronic structure data and to provide reliable estimates of the importance for nuclear dynamics, of the conical intersections we locate and characterize. To accomplish this a fully quantum mechanical time dependent wave packet program has been written based on the time-dependent Lanczos propagator,² a direct product representation of the vibrational wavefunction, and a distributed gaussian basis, although this last specification is easily changed. The basic matrix-vector multiply (\mathbf{Hv}) required by this algorithm, which is currently being parallelized, is made highly efficient by partitioning the N -mode direct product representation $D(N)$ into $D(m) \times D(N-m)$. This allows us to eliminate *a priori* all orthogonality required zeros for an m body term in the Hamiltonian, drastically reducing the cost of the matrix multiply. We anticipate results from this effort to emerge in the near future.

C. Diagnostics

The aim of the calculations described below was to determine absolute cross sections for the individual ro-vibrational levels of the *a-b* transitions in O₂ and NCl. These results were used by Skip Williams of AFGL as part of the calibration of an instrument to measure the concentration of O₂($a^1\Delta$). The results for NCl also described below will be used in a similar manner.

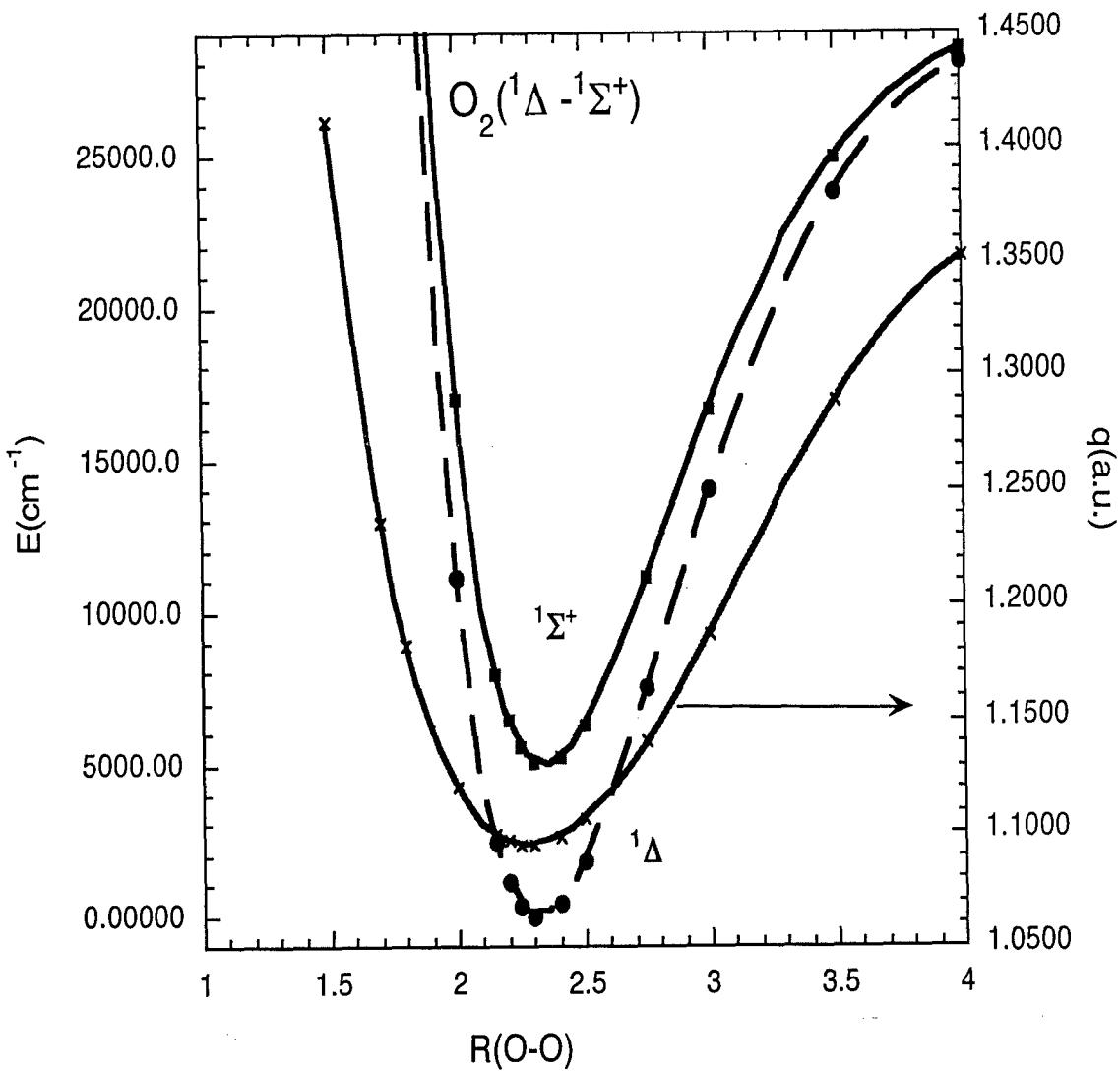
(i) Quantitative Detection of O₂($a^1\Delta$)

The $a^1\Delta - b^1\Sigma^+$ transition in O₂ is electric and magnetic dipole forbidden but has a nonvanishing electric quadrupole transition moment which carries the absorption. Our task was

divided into two parts: (i) obtain vibrationally averaged quadrupole transition moments of high accuracy for $a^1\Delta$ - $b^1\Sigma^+$ absorption; (ii) use these results to determine the absorption cross sections for individual ro-vibrational transitions. To accomplish part (i) we used second order AQCC (averaged quadratic coupled cluster) wavefunctions,³ an approximately size consistent variant of the multireference configuration interaction method as implemented in the COLUMBUS suite of programs. The molecular orbitals were obtained from a state-average complete active space MCSCF procedure that averaged the $a^1\Delta$ and $b^1\Sigma^+$ states and used the cc-pvqz basis set of Dunning ([12s6p3d2f1g]/(5s4p3d2f1g)). In part (ii) of our calculations the ro-vibrational Schrodinger equation was solved in the Hund's case-b limit. The solutions to the nuclear Schrödinger equation were used to construct the state-to-state quadrupole transition moments.

The potential energy curves produce intra state ro-vibrational energy levels within a few wave numbers of the experimental values and inter electronic state excitations good to ~ 100 cm⁻¹. This excellent level agreement with the available experimental data strongly supports the reliability of the transition moment calculation.

The electronic structure results, the $a^1\Delta$, $b^1\Sigma^+$ potential energy curves and quadrupole transition moment, are presented in the figure below:



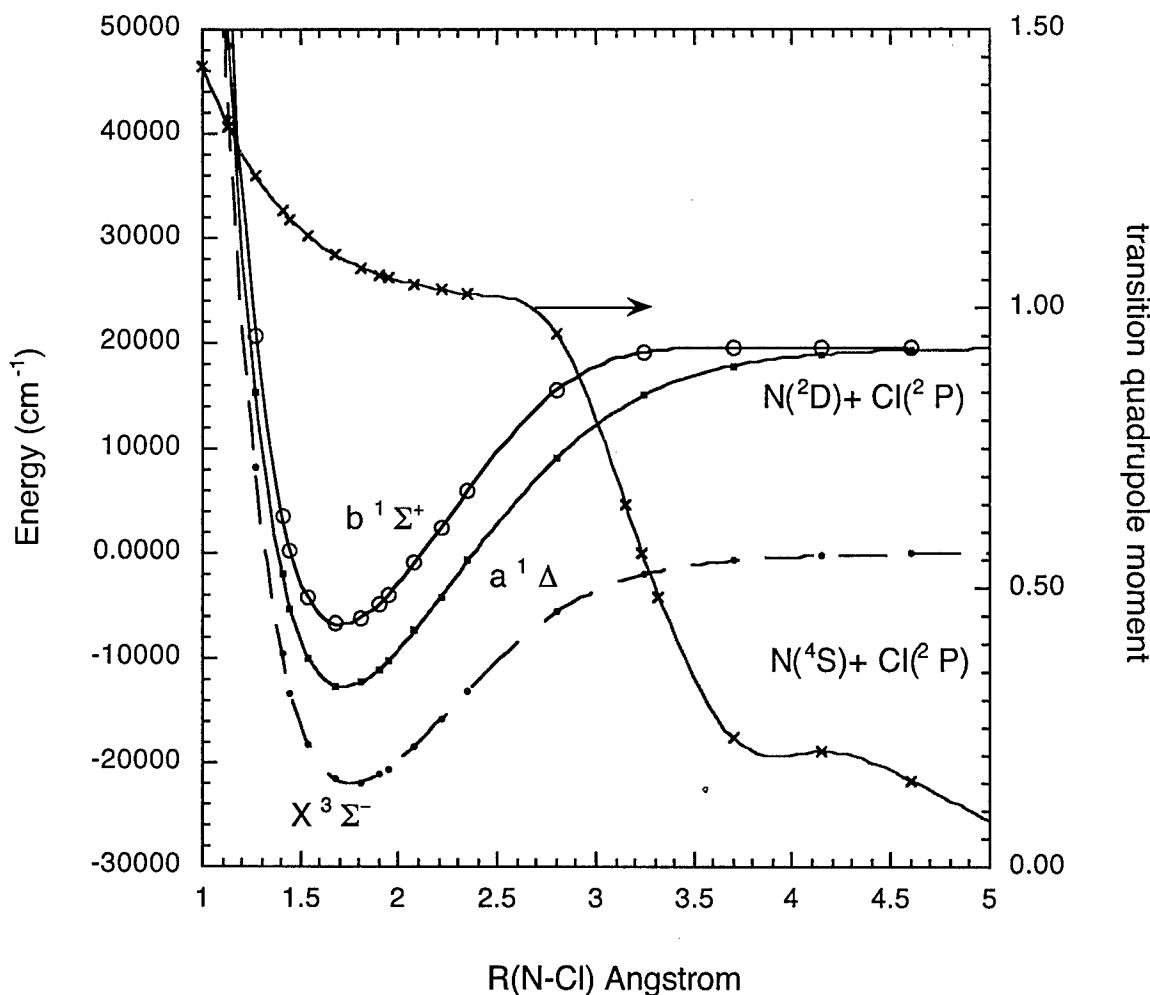
The use of these results to measure absolute $O_2(a^1\Delta)$ concentrations is described in Ref. ⁴. A detailed presentation of the electronic structure treatment and its use in the determination of the vibrationally averaged lifetimes is expected.

(ii) Quantitative Detection of $NCl(a^1\Delta)$

We have extended our theoretical treatment of the $a^1\Delta - b^1\Sigma^+$ absorption in O_2 (Ref. ⁴) to NCl . As was the case of O_2 , these results have been transmitted to Skip Williams of AFGL. He and his coworkers will use these results in the design of an instrument to measure the concentration of $NCl(a^1\Delta)$. As in the case of O_2 , the NCl $a-b$ transition is electric and magnetic

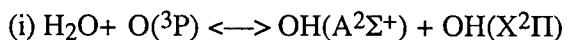
dipole forbidden but has a nonvanishing electric quadrupole transition moment which carries the absorption. Unlike the homonuclear O₂, for NCl the *a* and *b* states can decay via a spin-forbidden dipole-allowed mechanism to the X³Σ⁻ ground state. As part of earlier AFOSR funded research, we had determined the rates for these spin-forbidden processes⁵. Again we completed the NCl project, (i) obtaining quadrupole transition moments of high accuracy for *a*¹Δ - *b*¹Σ⁺ absorption, (ii) solving the corresponding vibrational Schrödinger equation to obtain vibrationally averaged transition moments and (iii) using these results to determine the absorption line strength. Again the second order AQCC approach was used, based on molecular orbitals obtained from a state-average complete active space MCSCF that averaged the *a*¹Δ and *b*¹Σ⁺ states. The active space was comprised of the 2s, 2p orbitals on nitrogen and the 3s and 3p orbitals on chlorine. The cc-PVQZ basis sets of Dunning were used. In the case of O₂ our potential energy curves for the *a* and *b* states produce intra state ro-vibrational energy levels within a few wave numbers of the experimental values and interstate excitations good to ~ 100 cm⁻¹. For NCl good agreement with the experimental results was also achieved. The computed T_e(*b*¹Σ⁺) of 15237 (14988) cm⁻¹ and ω_e(*b*¹Σ⁺) of 934 (936) cm⁻¹ and T_e(*a*¹Δ), of 9285 (9260) cm⁻¹ and ω_e(*b*¹Σ⁺) of 905 (905) cm⁻¹ are in good agreement with the experimental values given parenthetically. This level agreement with the available experimental data strongly supports the reliability of the transition moment calculation.

The electronic structure results, the *a*¹Δ, *b*¹Σ⁺ potential energy curves and quadrupole transition moment, are pictured below:

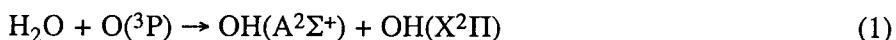


A detailed presentation of the electronic structure treatment and its use in the determination of the vibrationally averaged lifetimes is expected.

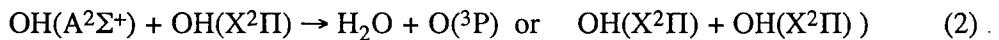
D. Nonadiabatic Processes in Atmospheric Chemistry



Vehicles in low-earth orbit travel at sufficiently high velocities that entrained molecules have enough kinetic energy to overcome substantial reaction endoergicities. One such reaction is the dissociation of water molecules by atomic oxygen to produce electronically excited OH(A²Σ⁺) which subsequently fluoresces. This reaction



is important in understanding the ultraviolet plume originating from the control engines of the space shuttle or the Soyuz engines of Russian service vehicles.[Gimelshein, 2000 #1604; Gimelshein, 2000 #1605; Gimelshein, 2001 #1603] First principles determination of the emitted radiation exhibit significant uncertainties, factors of 5-70, owing to the virtual absence of information concerning the vibrational distribution in the OH products. The back reactions, the reactive and non reactive quenching of OH(A²Σ⁺) by OH(X²Π)



may provide valuable insights into the mechanism of reaction 1. The reverse reaction is being studied by Marsha Lester's group and University of Pennsylvania. As a first step in estimating the reaction cross sections portions of the potential energy surfaces in question are used to determine the mechanism of reactions 1 and 2.⁶

It was found that these reactions are facilitated by seams of conical intersection that tie the 2,3²A potential energy surfaces correlating with O(^3P) + H₂O to the 5,6³A potential energy surfaces correlating with OH(X²Π) + OH(A²Σ⁺). The lowest energy points on the seams of conical intersection occur for collinear geometries, where they reduce to ³Π - ³Δ and ³Π - ³Σ⁺ symmetry-allowed seams of conical intersection. These conical intersections can be viewed as arising from the well-known HOH ¹Σ⁺ - ¹Π conical intersection perturbed by the ³Π component of O(^3P). Near their minimum energy points the ³Π - ³Δ and ³Π - ³Σ⁺ seams of conical intersection are separated by less than 90 cm⁻¹ suggesting that a subspace of the seam of conical intersections exists on which the (the C_s symmetry states correlating with the) ³Π - ³Δ and ³Π - ³Σ⁺ conical intersections coalesce into a single three state conical intersection. To explore this question an algorithm to locate conical intersections of three states of the same symmetry was developed.⁷ Although a coalescence was not found in this case, the algorithm was used to locate a three state conical intersection in polynitrogen compounds. The results from those calculations, described below are quite significant.

With regard to the forward reaction several factors favor the involvement of conical intersections. The conical intersection seams were shown to be accessible from both the reactant

and product channels without a barrier, above any reaction endoergicity. The seams occur at comparatively low energy relative to the products. Thus in the vicinity of these seams, the system will possess high kinetic energy and experience strong interstate couplings. The degeneracies required by collinearity reduce the number of isolated conical intersections, potential bottlenecks to upward transitions, that must be traversed to reach the products.

Analysis of the region between the products and the conical intersections has firmly established that these conical intersections will also play an essential role in the reverse reaction, where they provide for branching to either $\text{H}_2\text{O} + \text{O}$ or $\text{OH}(\text{X}) + \text{OH}(\text{X})$.

In the future it will be interesting to use the algorithms we are developing to study the dynamics of nonadiabatic transitions induced by conical intersections to obtain reliable estimates of the nonadiabatic transition probabilities near these conical intersections.

E. Conical Intersections and Energetics Materials

- (i) Three State Intersections radical species $(\text{CH})_{5-n}\text{N}_n$ $n = 1, 2, 3, 4$

This project was motivated by a talk given by W. C. Lineberger at the 2003 AFOSR Molecular Dynamics Program Meeting⁸ concerning the five member rings, $(\text{CH})_{5-n}\text{N}_n$ $n = 1, 2, 3, 4$. Interest in these molecules is due, at least in part, to the general interest in polynitrogen compounds as potential high performance rocket fuels.⁸

Our interest in these molecules concerns their spectroscopic signatures. While over the last decade conical intersections of two states of the same symmetry, once a theoretical curiosity, have come to be understood as essential players in photodissociation, conical intersections of three states of the same symmetry have been virtually ignored, despite the fact that they can have a profound affect on vibrational spectra. In a JACS communication we showed,⁹ using multireference configuration interaction (MRCI) wave functions comprised of 40 million configuration state functions (CSFs) that the ground state vibrational spectrum of $(\text{CH})_3\text{N}_2$ will be strongly perturbed by a three state conical intersection only $\sim 3400 \text{ cm}^{-1}$ above the lowest energy nuclear configuration! However more significantly, our calculations suggest that 3-state conical intersections of states of the same symmetry, virtually ignored in the past, are likely to exist in many organic radicals. We

predict that a doublet radical will have low-lying 3-state intersections provided: (i) there exists a low-lying LUMO and (ii) the highest doubly occupied molecular orbital is a nonbonding, lone pair, or similar orbital. This prediction, if fully confirmed, will require a rethinking, again, of our perception of ground state potential energy surfaces of organic radicals,

To test this hypothesis are studying the substituted cyclopentadienyl radicals, $(CH)_nN_{5-n}$ using large cc-TZP bases. The table below reports the results we have obtained from a consistent set of first order configuration interaction wave functions

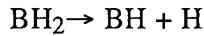
Molecule	E(ME3X)
C_4H_4N (pyrrolyl)	9292
$C_3H_3N_2$ (imidazolyl)	7955
$C_3H_3N_2$ (pyrazolyl)	4627
$C_2H_2N_3$ (1,2,4-triazolyl)	4101
$C_2H_2N_3$ (1,2,3-triazolyl)	4028
CHN_4 (tetraazolyl)	5589

Here E(ME3X) represents the energy (in cm^{-1}) of lowest three state conical intersection relative to ground state minimum. All the radicals in question clearly exhibit three state degeneries. Further, on the basis of our earlier pyrazolyl results we anticipate that more accurate second order wavefunctions will lower the predicted energy of the three state degeneracies by ~ 1000 cm^{-1} . Thus the triazolyl geometric isomers exhibit particularly low-lying three state intersections. We believe these results serve to identify a general class of doublet radicals for which three state intersections will play an important role and go a long way to demonstrating the prevalence of three state conical intersections.

Once these intersections have been located and characterized, we will develop three electronic state vibronic coupling hamiltonians.¹⁰ These hamiltonians will be used to determine the high resolution vibronic spectra that have proved difficult to interpret. One particular advantage of

the theoretical approach is that it will permit us to include the interstate couplings one state at a time thereby obtaining valuable insights into the effects of three state intersections on vibronic spectra.

(ii) A Benchmark system: The potential energy, derivative coupling, surfaces for $B(^2P) + H_2 \rightarrow$



The captioned reaction is relevant to the combustion of boron doped cryogenic H_2 . In collaboration with David Weeks of AFIT, high quality *ab initio* potential energy, and derivative coupling, surfaces have been constructed as a prelude to the study of the dynamics of the captioned reaction. A unique aspect of the electronic structure problem was the need for a functional representation of the energies and derivative couplings in the vicinity of a seam of conical intersections with intersecting branches. This problem was solved by using perturbation theory as described in Ref. ¹¹.

With the electronic structure data in hand we have turned to the question providing a diabatic representation of these potential energy surfaces and their interactions including a precise determination of the residual derivative coupling.¹² In addition to the relevance of the captioned reaction to the combustion of cryogenic H_2 the resulting potential energy, and interstate coupling, surfaces will provide a unique benchmark in the study of nonadiabatic processes.

F. Future Directions

(i) Conical intersections and energy transfer relevant to chemical iodine laser systems

In the theoretical description of energy transfer reactions relevant to chemical laser systems based on the $I(^2P_{1/2}) \rightarrow I(^2P_{3/2})$ transition, the spin-orbit interaction must be taken into account. However the treatment of the spin-orbit interaction is complicated by the existence of conical intersections connecting the relevant potential energy surfaces and the need to properly account for time reversal symmetry. These issues are frequently treated in an approximate manner. Over the last three years we have developed the formal tools¹³ necessary to deal with these issues in a rigorous manner. Computer programs to treat this problem in systems with low atomic number (low Z) atoms have been developed. One of the goals of our future research will be to use this formalism to extend the low Z methodology to systems with large spin-orbit splittings.

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4. *Determination of potential energy surface intersections and derivative couplings in the adiabatic representation* David. R. Yarkony, in **Conical Intersections: Electronic Structure, Dynamics and Spectroscopy**, Wolfgang Domcke, David R. Yarkony and Horst Köppel, eds. *World Scientific Publishing, Singapore*, (2004)
5. *Quantitative Detection of Singlet O_2 via Cavity Enhanced Absorption*
Skip Williams, Manish Gupta, Thomas Owano, Douglas S. Baer, Anthony O'Keefe, David R. Yarkony, and Spiridoula Matsika, *Optics Lett.* **29**, 1066-1068(2004)
6. *A Continuous Representation of the Branching Spaces of Two State Conical Intersections Along their Seams. A Group Homomorphism Approach*, S. Han and D. R. Yarkony, in **Conical Intersections**, G. Worth and S. Althorpe, eds. (CCP6, 2004)

PERSONNEL

The following scientists in my research group have contributed to work reported herein.

Postdoctoral Research Associates	Principal Investigator(PI)
Dr.Spiridula Matsika (July, 2000-July 2003)	Professor David R. Yarkony
Dr. Michael Schuurman (Jan. 2005 -)	
Graduate Students	
Mr. Richard Young (July, 2002-	
Mr. Joseph Dillon (Jan. 2005-	

INTERACTIONS/TRANSITIONS

Invited Presentations

Below are listed invited talks given by the PI based on work performed as part of this grant

1. *Conical Intersections Beyond Diabolical*
Atomic and Molecular Interaction Gordon Conference, Bristol RI July 2002
2. *Higher Dimensional Conical Intersections,*
Conference on Highly accurate Potential energy surfaces
University College London, 31- May – 3 April 2003
3. *Higher Dimensional Conical Intersections. Beyond Diabolical*
COMET, Madrid, Spain June 2003
4. *Beyond Two Dimensional Cones,*
Gordon Conference on Molecular Energy Transfer, Granlibakken CA, July 2003
5. Marching along ridges
Faraday Discussions 127, Oxford England April 2004
6. Seams of Conical Intersection are more than isolated points
Symposium Honoring N. C. Handy Cambridge, England July 2004
7. Conical Intersections and the Chemical Iodine Lasers
AFIT, Dayton, OH Aug. 2004
8. Statistical vs Nonstatistical Photodissociation; The Role of Conical Intersections
National ACS Meeting, Philadelphia, PA Aug 2004
9. Higher Dimensional Conical Intersections
Quantum Dynamics at Conical Intersections, Nunspeet, Netherlands, Sept 2004

Transitions

Ro-vibrational quadrupole transition moments for the O₂ and NCl *b-a* transitions (as described herein) and associated theory have been provided to Skip Williams of AFGL

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13. ABSTRACT (Maximum 200 Words) There are three particularly notable aspects to this AFOSR sponsored work. The work with most enduring impact is our study is on the polynitrogen molecules, $(CH)_nN_{5-n}$ $n = 1, 2, 3, 4$. We found that these molecules have complicated photoelectron spectra owing to the existence of low-lying conical intersections or three states with little or no symmetry. Further this study identified a whole class of doublet radicals that are expected to exhibit low-lying three state conical intersections. In the past three state intersections had been virtually ignored as too rare to be of consequence. Thus these findings require a re-thinking of both the prevalence of three state conical intersections and the electronic structure of a commonly occurring class of reactive chemical species. Secondly, we have made the electronic structure tools we have developed to locate and analyze two and three state conical intersections freely available to the general scientific community through the COLUMBUS suite of electronic structure codes. These extremely efficient multireference configuration interaction based codes are currently being maintained and extended through the combined efforts of Lischka (Vienna) and Sheppard (Argonne). Finally there is our theoretical determination of the absorption cross section for the $a-b$ transitions in O_2 and NCl . We were able to perform these highly accurate theoretical calculations, which are relevant to the energy transfer iodine laser systems, in a timely manner because of our participation in the AFOSR theoretical chemistry program.		
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